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Observation by Optically Detected Magnetic Resonance of Frenkel Pairs in Irradiated ZnSe

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Optical detection of magnetic resonance is reported for three distinct zinc-vacancy–zinc-interstitial Frenkel pairs in ZnSe produced by 2.5-MeV electron irradiation at 4.2 K. One is detected as distant-donor-to-Frenkel-pair recombination in luminescence at ~600 nm. The other two are detected as localized-triplet recombination luminescence at ~800 nm. The emitting excitonic state is analyzed as a hole on the zinc vacancy with an exchange-coupled electron on the nearby interstitial zinc. From this, the EPR properties of the isolated interstitial zinc donor are deduced.

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The Frenkel pair—an interstitial host atom trapped near its vacant lattice site—can be considered the fundamental lattice excitation of a perfect crystalline solid. It plays the same central role for the *lattice* structure that the exciton—a bound electron-hole pair—plays as the fundamental excitation for the *electronic* structure of the solid. In this Letter, we report optical detection of magnetic resonance (ODMR) of three distinct zinc-vacancy–zinc-interstitial Frenkel pairs in ZnSe (differing in the separation between the constituents). We believe that this represents the first unambiguous identification of an optical transition associated with this fundamental defect in any solid.

Frenkel pairs have previously been identified in ZnSe by electron paramagnetic resonance (EPR).[1,2] In those studies five distinct $S=\frac{1}{2}$ centers, labeled V, V^{I}, V^{II}, V^{III}, and V^{IV}, were observed after 1.5-MeV electron irradiation at 20.4 K. V was identified as arising from a hole trapped at the isolated zinc-lattice vacancy (V^-) and the others as zinc-vacancy hole centers each perturbed by a nearby interstitial Zn^{++} ion in a different nearby lattice position. From the symmetry of the spectra, their behavior under uniaxial stress, their alignment versus beam direction, and their annealing properties, specific Frenkel-pair models were suggested for several of the centers.

The isolated vacancy was found to be stable at room temperature, making it possible to identify its optical properties unambiguously by optical detection of magnetic resonance in both luminescence[3,4] and absorption.[5] From these studies, a detailed understanding of the electronic structure of the isolated vacancy has emerged. However, the Frenkel pairs are not stable above cryogenic temperatures and the experimentally more difficult *in situ* ODMR studies have not previously been attempted. Several luminescence bands have been reported in ZnSe after *in situ* electron irradiation at cryogenic temperatures[6-9] which anneal in the same general temperature region as the close pairs seen in EPR. This was noted in the early EPR studies and a tentative identification of these bands with the zinc-lattice Frenkel pairs was suggested.[1,2,10] It was pointed out that these pairs might be very efficient luminescence centers because of the charge compensation of V^- by the positively charged nearby zinc interstitial. In this Letter, we describe *in situ* ODMR experiments on these luminescence bands.

We have modified the cryostat of the 20-GHz EPR spectrometer used in our previous EPR *in situ* irradiation studies[11] to provide the required optical access. The sample was immersed in liquid helium and irradiated by 2.5-MeV electrons to a fluence of $\sim 5\times10^{16}$ e/cm^2. It was then lowered to the center of a TE_{011} microwave cavity and the helium pumped below the λ point ($T\sim1.5$ K). Optical excitation of 5 mW was provided by the 458- or 476-nm line of an argon-ion laser through an optical fiber terminating at a point in the cavity just above the sample. This fiber was threaded through a concentric quartz capillary tube ($\sim\frac{3}{16}$ in. diam ×48 in. long) which served in turn as a light pipe to guide the luminescence out of the cryostat to an external detector. The incident microwaves ($\sim$25 mW) were chopped with a ferrite modulator at 2 kHz and the synchronous changes in emission intensity were detected in the direction perpendicular to the magnetic field by means of a silicon photodiode (EGG 250 UV) for the visible radiation or a cooled germanium detector (North Coast EO-817) for the near-infrared radiation.

The sample studied was a single crystal grown by vapor transport in a sealed quartz ampoule. After purification by "zinc extraction" (fired in liquid zinc for 70 h at 900 °C, and then quenched to room temperature), the material was low-resistivity n type with an uncompensated donor concentration of $\sim 9\times10^{16}/\mathrm{cm}^3$ as determined by Hall measurements. The sample was mounted so that irradiation could be performed with the e^- beam approximately parallel to either the [111] or the $[\bar{1}\bar{1}\bar{1}]$ direction.

In Fig. 1, the luminescence before and after *in situ* irradiation is shown after correction for monochromator and detector response. After irradiation, the luminescence intensity has increased greatly, revealing broad bands at ~600 and ~800 nm. The band at 600 nm is preferentially excited with 458-nm excitation, and the band at 800 nm, with 476-nm excitation.

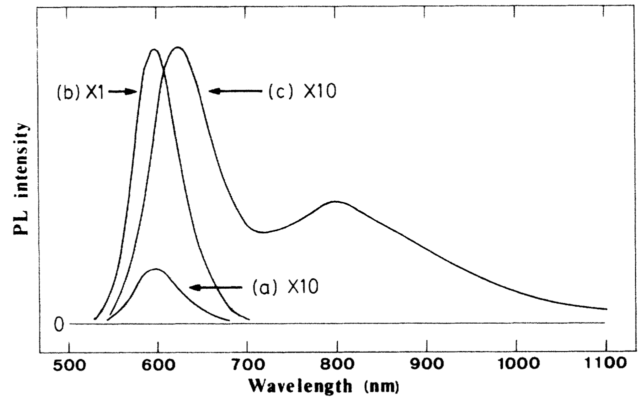

FIG. 1. Photoluminescence spectra at 4.2 K of ZnSe (curve *a*) before and (curves *b,c*) after *in situ* 2.5-MeV electron irradiation. Spectra *a* and *b* were taken with 5 mW of 458-nm excitation, and spectrum *c*, with 5 mW of 476-nm excitation.

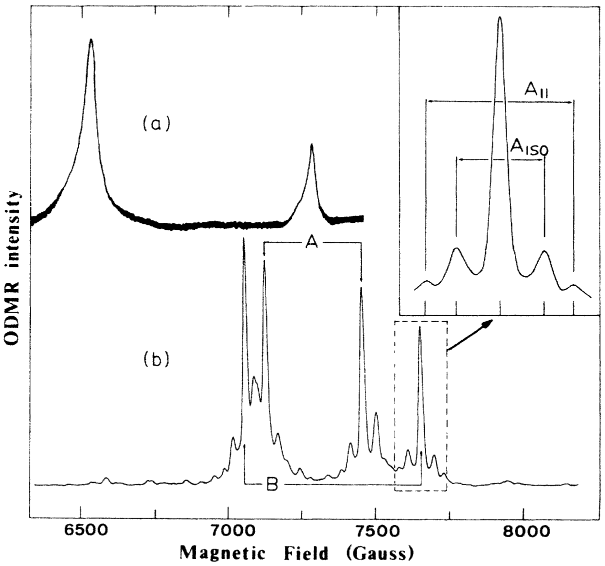

FIG. 2. ODMR spectra (**B**$\parallel\langle 111\rangle$, $T\sim 1.5$ K, $\nu\sim 20$ GHz) in ZnSe after *in situ* 4.2-K electron irradiation. (a) Spectrum detected near $g\sim 2$ in the 600-nm band; 458-nm excitation. (b) Spectra detected in the 800-nm band; 476-nm excitation.

With selection of the 600-nm band with a tunable interference filter (Oriel Model 7155), ODMR reveals a strong isotropic signal at $g\sim 1.109\pm 0.001$ identified with shallow donors,[12,13] and a weaker complex anisotropic set of lines near $g=2$ which are shown in Fig. 2(a). The angular dependence of these lines (shown dashed in Fig. 3) reveals a $\langle 111\rangle$ axially symmetric $S=\frac{1}{2}$ center with the g values given in Table I. These g values are identical within experimental accuracy to those observed by EPR[2,3] for the V^{I} Frenkel pair, for which the dislodged Zn atom was deduced to be located in a nearby $\langle 111\rangle$ interstitial position. The 600-nm luminescence and the V^{I} ODMR signal disappear after 15-min isochronal annealing at ~ 80 K in agreement with the V^{I} EPR results. Also, strong preferential formation of the ODMR centers aligned along the irradiation beam direction is observed, in close correlation with the EPR observations. We conclude therefore that the 600-nm luminescence arises from radiative

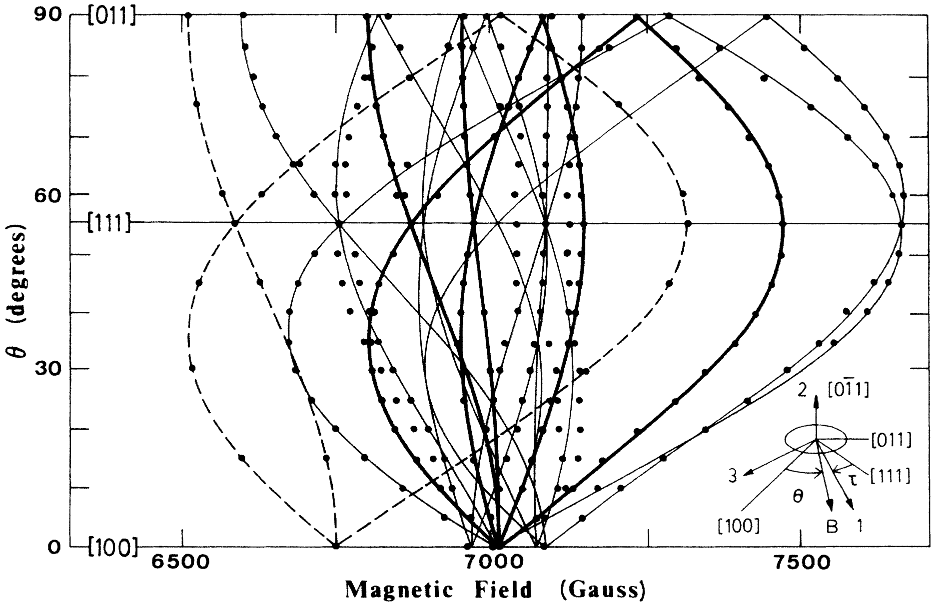

FIG. 3. Angular dependence of the ODMR lines, **B**$\perp$[0$\bar{1}$1]. The curves are calculated with use of the spin-Hamiltonian parameters given in Table I. (V^{I}, dashed lines; A, heavy solid lines; B, light solid lines.) Inset: The principal axes of one of the equivalent defect orientations for each spectrum.

TABLE I. Spin-Hamiltonian parameters for spectra V^{I}, A, and B. (See Fig. 3 for defect axes; D and A are given in units of 10^{-4} cm^{-1}.)

Parameter \ Spectrum	V^{I}	A(V^{IV})	B(V^{III})
S	$\frac{1}{2}$	1	1
g_1	1.961(1)	1.954(1)	1.939(1)
g_2	2.205(1)	2.078(2)	2.081(2)
g_3	2.205(1)	2.078(2)	2.075(2)
$\tau_g(\pm 1°)$	0	0	0
D_1	$\cdots$	$\pm 98(2)$	$\pm 178(2)$
D_2	$\cdots$	$\mp 49(1)$	$\mp 178(2)$
D_3	$\cdots$	$\mp 49(1)$	0(2)
$\tau_D(\mp 1°)$		0	-10
$\lvert {}^{77}A_{\parallel} \rvert$	$\cdots$	135(10)	135(10)
$\lvert {}^{77}A_{\mathrm{iso}} \rvert$	$\cdots$	75(5)	75(5)

recombination between an unperturbed distant donor and the V^{I} Frenkel pair, according to the decay scheme

$$D^0 + V_{\mathrm{Zn}}^{-}\,\mathrm{Zn}_i^{++} \longrightarrow D^{+} + V_{\mathrm{Zn}}^{--}\,\mathrm{Zn}_i^{++} + h\nu. \qquad (1)$$

This explains the observation of the $S=\frac{1}{2}$ resonances of both the donor (D^0) and the V^{I} Frenkel pair ($V_{\mathrm{Zn}_i}^{-}\,\mathrm{Zn}_i^{++}$) in the excited emitting state.

Two additional strong anisotropic spectra were detected in the 800-nm band. These are shown in Fig. 2(b). They are strongest with the magnetic field along the [111] direction, their intensities falling rapidly as the magnetic field is rotated away. They remain intense enough, however, to follow through most of the $(0\bar{1}1)$ plane and the angular dependence deduced is shown in Fig. 3. The solid lines represent the calculated values for two distinct $S=1$ spectra, with spin Hamiltonians

$$H=\mu_{\mathrm{B}}\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}+\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}+\sum_j \mathbf{S}\cdot\mathbf{A}_j\cdot\mathbf{I}_j. \qquad (2)$$

The spin-Hamiltonian parameters for the spectra, labeled A and B, are given in Table I. For each spectral line, satellite structure is resolved, Fig. 2(b), which we identify as arising from hyperfine interaction with ^{77}Se ($I=\frac{1}{2}$, 7.5% abundant). The outermost satellites correspond in relative intensity to interaction at a single Se site. They are resolved only for **B** approximately parallel to $\langle 111\rangle$ and the A value is recorded in Table I as $^{77}A_{\parallel}$. $^{77}A_{\mathrm{iso}}$ in the table refers to the inner satellites which show no variation with orientation and correspond in intensity to approximately four equivalent selenium sites.

An important clue to the interpretation of these $S=1$ spectra is the observation that the anisotropy of **g** and the value of $^{77}A_{\parallel}$ are very close to one half those for the isolated zinc vacancy.[3] From this we conclude that the luminescence in each case is from a triplet excitonic state of a defect involving an $S=\frac{1}{2}$ hole on the zinc-lattice vacancy, and an $S=\frac{1}{2}$ exchange-coupled electron which resides nearby. For such a system, the g and A values should reflect the *average* of the separated electron and hole values, similar to that recently reported for the triplet state of copper–near-neighbor donor pairs in CdS.[14] Annealing studies reveal that spectrum A disappears at ~140 K and spectrum B at ~180 K, along with the 800-nm band, in close agreement with the EPR observation for V^{IV} and V^{III}, respectively. The symmetries of the spectra A and B coincide with those determined for the $S=\frac{1}{2}$ V^{IV} (near axial) and V^{III} (C_{1h}) EPR spectra, respectively. (No detailed model was proposed for V^{IV} in the EPR studies, but V^{III} was deduced to have the zinc interstitial displaced in a $\langle 100\rangle$ direction from the vacancy.) Strong preferential orientation of both ODMR spectra are observed versus e^- beam direction, also in direct agreement with the EPR observations.

We conclude therefore that the nearby electron trap is the interstitial zinc atom and that the 800-nm luminescence arises from a localized "charge transfer" or excitonic transition in which

$$V_{\mathrm{Zn}}^{-}\,\mathrm{Zn}_i^{+} \longrightarrow V_{\mathrm{Zn}}^{--}\,\mathrm{Zn}_i^{++} + h\nu \qquad (3)$$

at the V^{IV} (spectrum A) or V^{III} (spectrum B) Frenkel pair, respectively.

With this identification we can, in turn, deconvolute the spectrum to estimate the EPR properties associated with the interstitial Zn$^+$ state. Since the g values should be the average of that for the hole on the vacancy and that for the interstitial zinc, we obtain an isotropic value $g_{\mathrm{Zn}^+} \cong 1.95$.

The closer-in satellites in Fig. 2(b) correspond in intensity to approximately four equivalent selenium sites and appear isotropic Since no similar satellites are observed for the zinc vacancy,[3] we tentatively identify them as arising from the four nearest-neighbor selenium atoms surrounding the interstitial zinc. The $A_{\mathrm{iso}}=75\times10^{-4}$ cm^{-1} corresponds to an isotropic $A=150\times10^{-4}$ cm^{-1} for the four nearest selenium neighbors associated with the $S=\frac{1}{2}$ electron on the interstitial zinc. This is an important bit of information, because it appears to confirm that the zinc is in the interstitial site surrounded by four Se atoms (rather than the ionically less stable site surrounded by zinc atoms, which also must be considered as a possible site in low-temperature production studies).

The fine-structure term **D** potentially contains important additional information about the defect. In the limit, for instance, of very weak overlap between electron and hole, the term should originate primarily from magnetic dipole-dipole interaction between the two particles, providing, in turn, an estimate of the distance of the interstitial from the vacancy. For example, the **D** for spectrum A indicates a dipole-dipole separation of 5.5 Å (in rather close agreement with the distance between the closest ⟨111⟩ stable interstitial zinc site and its vacancy, which is 4.9 Å). On the other hand, the large anisotropy of **D** for spectrum B is difficult to understand in terms of dipole-dipole interactions alone, suggesting the contribution also of spin-orbit interaction at intermediate sites of overlapping electron and hole wave functions. Further studies will be required before a reliable interpretation of the **D** term is possible.

In conclusion, we have identified by ODMR studies the luminescence associated with three distinct zinc-vacancy–zinc-interstitial Frenkel pairs in electron-irradiated ZnSe. The least-stable pair V^{I} is seen in distant-shallow-donor to deep-Frenkel-pair (actually also a donor) recombination luminescence at 600 nm. The other two pairs, V^{III} and V^{IV}, are seen in an excitonic or charge-transfer recombination at 800 nm in which an electron on the nearby interstitial recombines with a hole on the zinc vacancy. No signals have been observed that are associated with the fourth Frenkel pair detected by EPR (V^{II}).

The apparent two-particle character of the triplet excited states has allowed us to deduce in addition the EPR properties of the zinc interstitial. To our knowledge, this represents the first EPR or, in fact, any spectroscopic information concerning an intrinsic host interstitial atom in any semiconductor.

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